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INTRODUCTION

When residual oil is burned, the sulfur it contains can cause many problems. These include pollution and localized problems of gas-side corrosion and deposition which can be especially severe when the fuel is burned in modern boilers which have heat recovery equipment. The additives and treatment programs discussed in this paper are designed to alleviate the localized problems.

Sulfur dioxide (SO_2) and sulfur trioxide (SO_3) are considered harmful pollutants, and acidic rain in which these gases are dissolved is aggressive to construction materials. Recently there has been much concern about the environmental effects of sulfates, which comprise the major part of the end products of sulfur oxides in the environment. (1) It is highly unlikely that a simple additive approach can remove enough sulfur oxides from flue gases to effectively alleviate the general SO_x pollution problem. Approaches which are now under active investigation by various companies and agencies include fluidized-bed combustion in a bed of limestone, dry limestone furnace injection, fuel pretreatment and wet scrubbers. (2, 3, 4, 5)

Localized corrosion, deposition and pollution problems can, however, be treated by an additive approach. These problems are all caused by acid condensation and commonly occur on the gas-side of the cold ends of boilers. The cold end of a boiler consists of the economizer, air heater, particle collection equipment and stack (Figure 1). Flue gas temperatures in this area typically range from 1200F to 200F. The air heater, where flue gas temperatures typically range from 600F to 350F, is the most common trouble spot. Sulfuric acid condenses on surfaces which are below the acid dewpoint and results in corrosion of those surfaces; resultant sticky deposits and exfoliated corrosion products can block the gas flow. Acid smut, which consists of soot particle agglomerates which have absorbed sulfuric acid, probably also forms on cooled surfaces. Emission of this material causes a major local pollution problem. In addition, hygroscopic, acidic fly ash is difficult to handle for disposal.

The cold-end additives developed by the work described here were developed to alleviate the problems of cold-end corrosion, cold-end fouling, acidic fly ash and acid smut. They will adsorb or react with SO_3 or sulfuric acid, rather than SO_2 .

By allowing boilers to run at lower exit gas temperatures without excessive cold-end problems, these additives should increase boiler efficiency and help save fuel.

The mechanism by which these materials alleviate cold-end problems was investigated and the influence of properties such as basicity, adsorptivity and particle size on additive effectiveness was studied. Knowledge of these factors is necessary to formulate and apply cold-end additives most efficiently.

Additive materials having a wide variety of properties were studied and are listed in Table I. Most were highly alkaline, but activated alumina and expanded vermiculite were moderately alkaline and were expected to be highly adsorptive; silica was expected to perform by adsorption alone. The particle size of all materials except sodium aluminate, sodium carbonate and vermiculite was 325 mesh or smaller. All of the materials are stable at cold-end temperatures except ammonium bicarbonate, which decomposes to yield ammonia, carbon dioxide and water.

TEST METHODS

Tests were conducted on three utility boilers and two industrial boilers, which ranged in capacity from 150,000 to 4,000,000 pounds of steam per hour. The utility boilers were equipped with Ljungstrom air heaters, and the industrial units had shell-and-tube air heaters. All were fired with no. 6 oil, with sulfur contents between 0.9 and 2.5 percent.

Additives were fed to points between the boiler economizers and air heaters where sufficient turbulence existed to insure even distribution across the duct. Test points were either upstream or downstream of the air heaters but were at least 10 feet downstream of the injection points. Additives were metered into pipes or headers leading to the ducts by a feeder consisting of a vibratory funnel and a vibrating trough, which was calibrated periodically using each additive. The additives were conveyed to the duct by gravity, boiler draft and when necessary, compressed air.

Tests were conducted to learn how additives affect acid deposition on surfaces. The rate of acid deposition was determined vs. surface temperature using a probe based on the British Central Electricity Research Laboratories (CERL) acid deposition probe.⁽⁶⁾ The probe washings were also analyzed for iron and total solids, which indicated corrosion rate and fouling tendency, respectively. Surface coverage was noted visually. An independent, indirect measure of acid deposition rate was obtained from a Land Instruments dewpoint meter, a commercial instrument. Gas flow rates and sulfur trioxide and sulfur dioxide concentrations in the flue gases were determined using a Research Appliance Corporation model 2343 stack sampling train.

The CERL probe was a stainless steel pipe, divided by rings into equal areas. A thermocouple was embedded in each area, and the pipe was fitted with an air-regulating valve. This probe was inserted in the boiler flue and cooled with compressed air. A temperature gradient along the length of the probe was obtained and recorded using the thermocouples. After exposure for a certain time, each area was washed with water, the washings were collected in separate bottles and titrated as sulfuric acid to determine the rate of acid deposition.

When using the Land meter, condensation of a conducting film of condensed acid on a controlled-temperature probe tip was detected by the onset of electric current flow between electrodes embedded in the tip. This allowed the apparent dewpoint to be determined, and comparative rates of acid build-up (RBU) were obtained from the rate of increase in current with time at any tip temperature.

The mechanism of cold-end protection by additives was discovered accidentally. Initial tests showed that additives had no effect on sulfur oxide concentrations in the flue gases. Additives were later found to reduce acid deposition on surfaces by coating these surfaces.

The test unit (Unit A) was a modern, front-fired utility boiler which was rated for 950,000 pounds of steam per hour. It was originally designed to burn pulverized coal, but was later converted to fire oil; specifically, it fired oil containing about 2.2 percent sulfur. As a result, the air heaters, which had been initially sized to handle large amounts of fly ash emanating from coal combustion, were improperly sized for flue gas from oil firing. The resulting low temperatures caused acid smut formation and a potential for acid corrosion.

Various blends of ammonium bicarbonate, adsorbents and alkaline solids were injected upstream of the air heaters to try to neutralize SO_3 , but they had no effect on flue gas sulfur oxide concentrations or on the pH of fly ash from the precipitator hoppers. The mixing and residence times apparently were insufficient to effectively remove sulfur trioxide.

A second trial determined the effects of the additives on acid deposition on cooled surfaces. The additives were again injected into a turbulent area upstream of the air heater, and acid deposition rates were determined downstream of the air heater with the CERL probe. The additives were an alumina-silica mixture and an ammonium bicarbonate-silica mixture. At this time the plant had switched to a low-sulfur oil containing one percent sulfur.

Both additives effectively reduced acid deposition over a wide range of feedrates, as can be seen in Table II. The maximum additive: sulfur trioxide mole ratios represented by the feedrates in Table II were below 0.5:1 for both alumina and ammonia, as calculated from the measured flue gas flow rate and sulfur trioxide concentration. Stoichiometric reaction with SO_3 would have required additive: sulfur trioxide mole ratios of 0.33:1 for Al_2O_3 and 2:1 for ammonia.

The additives thus essentially eliminated acid deposition at dosages which were as low as one-fourth of stoichiometric, and reduced acid deposition at lower dosages. This fact, along with the negligible effect on bulk SO_3 concentration and the observation that a brief conditioning period was needed before the additive effects were seen, indicated that protection was resulting from coating the probe surface with additive rather than from reacting with the bulk of the sulfur trioxide. Ammonium bicarbonate apparently maintained its integrity long enough to reach the surfaces. It was thought that cold-end surfaces would be protected in the same way, and patent coverage⁽⁷⁾ was obtained for these additives.

There are several benefits of protection by surface coating. First and most obvious, a minimal amount of additive is needed since only the acid which condenses on surfaces is neutralized or adsorbed. Second, injection points can be chosen to solve specific problems such as air heater

corrosion or acidic, sticky ash in precipitator hoppers. Third, there is minimal effect on scrubbers or precipitators downstream since the bulk of the flue gas is unchanged.

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CONFIRMATION

The beneficial effects of the additives applied in the manner described above were confirmed in trials at two utility boilers. Unit B burned no. 6 oil containing approximately 0.9 percent sulfur and produced 500,000 pounds of steam per hour; Unit C, fired with a blend of no. 2 and no. 6 oils containing about 1.2 percent sulfur, produced up to 4,000,000 pounds of steam per hour.

An ammonium bicarbonate-silica mixture effectively reduced acid deposition on the CERL probe in unit B at $\text{NH}_3:\text{SO}_2$ mole ratios of 1:1 and 0.5:1 (Figure 2). An alumina-silica mixture reduced the acid deposition rate on the CERL probe by approximately 50 percent and the initial corrosion rate of the probe by 30 percent in Unit C.

Further, indirect confirmation of the surface coating mechanism was provided by a partial failure in Unit D, an industrial power boiler which burned oil containing about 2.5 percent sulfur and produced approximately 600,000 pounds of steam per hour. The configuration of the shell-and-tube air heater is shown in Figure 3. Gas-side corrosion was occurring at the cold end of the air heater. An alumina-silica mixture was fed upstream of the air heater. Space limitations prevented CERL probe tests at the cone, but tests with the Land meter (Table III) showed that the alumina-silica additive depressed the apparent dewpoint and reduced the acid condensation. CERL probe tests at the cold-end of the air heater, however, showed no difference between treated and untreated flue gases. It was apparent that the additive was being lost in the 180-degree bend.

CORROSION TEST

The effectiveness of the alumina-silica mixture was confirmed by corrosion rate determinations in the cold end of a boiler producing 470,000 pounds of steam per hour (Unit E). Unit E fired blast furnace gas as primary fuel and coke oven gas and no. 6 oil as secondary fuels.

A corrosion specimen probe was constructed (Figure 4) and exposed to the flue gases after the air heater for 30 days without additive, and then for 30 days with the alumina-silica mixture being fed at a rate of six parts per million (ppm) by weight of flue gases. The surface temperature was 140F; the corrosion rate for the control, determined by specimen weight loss, was 52 mils per year (mpy). The corrosion rate for the treated gases was 32 mpy.

Visual inspection showed most corrosion to be on the downstream side of the specimen, which was inserted perpendicular to the gas flow. The additive had coated the leading surface of the specimen and effectively prevented corrosion.

ADDITIVE PROPERTIES

Once the surface coating mechanism was established, the effect of chemical and physical properties on cold-end additives was investigated. The

properties considered were alkalinity, adsorptivity and particle size.

The additives listed in table I were evaluated in an industrial boiler (Unit F) with a capacity of 150,000 pounds of steam per hour. The oil burned at this plant contained approximately 2.2 percent sulfur, and gas-side corrosion had caused perforation of the air heaters.

Only fine materials covered the CERL probe evenly, as visual inspection of the probe (Table IV) determined. This was confirmed by erratic acid deposition results for the coarse materials. For example, acid deposition rates for sodium aluminate differed by a factor of more than three. Such uneven coverage of cold-end surfaces would result in unreliable protection from acid attack and would lead to the danger of fouling air heaters before all surfaces were covered.

All five materials provided some protection, including one which did not neutralize the condensed acid.

Acid deposition rates on the CERL probe are shown in Figures 5 and 6, and rates of acid build-up on the Land meter are shown in Figure 7.

Figures 5 and 6 show that at high feedrates the alkaline materials MgO and $Ca(OH)_2$ were superior to the mildly alkaline $Al_2O_3-SiO_2$ combination; at lower feedrates all these materials were roughly equivalent. It may be that at high feedrates the basic oxides achieve some benefit from reacting with the bulk SO_3 , while at lower dosages surface-coating alone is operable and the materials are equivalent.

Figure 7 indicates that silica, which had no effect on acid deposition as measured by the CERL probe (Figure 5), did provide surface protection. Adsorbed but unreacted acid could be titrated in the CERL probe washings as free acid. The electric current increase measured by the dewpoint meter, however, depends on the formation of a continuous film on the probe tip. Adsorption by a non-conducting solid would prevent this.

Silica apparently did adsorb the condensing acid. Such adsorption would protect the surfaces by preventing contact with the acid. This was confirmed in an experiment when corrosion of the CERL probe (estimated from iron in the washings) was reduced 50 percent by allowing the probe to be coated by SiO_2 -treated flue gases for 90 minutes before starting the cooling air. The adsorptive, mildly alkaline alumina-silica combination looks especially good in Figure 7.

These additives do not cause fouling when applied properly. Analysis of CERL probe washings for total solids showed no increase in deposited solids in the presence of the additives: the reduced stickiness of the treated deposits probably counteracted the increased solids loading in the flue gases.

All the materials tested appear practical, except possibly calcium hydroxide which forms insoluble sulfates.

1. Cold-end surfaces may be protected by surface coatings of materials added directly to the cold end.
2. Protection by surface-coating offers advantages of economy and flexibility.
3. Fine particle size is essential in cold-end additives.
4. High adsorptivity and at least moderate alkalinity are desirable in cold-end additives.
5. Aluminum oxide, ammonium bicarbonate, magnesium oxide and silica are among the suitable materials for powdered cold-end additive constituents.

CURRENT PROGRESS

Blends of the various materials investigated in this study are available commercially. To insure maximum protection, suppliers must have expertise in additive application.

New materials now being tested include liquids, which should be especially convenient, and specific corrosion inhibitors.

With cooperation between boiler owners and operators and experts in fuel treatment, progress in energy conservation, equipment reliability and environmental quality can be furthered. Specifically, cold-end additives allow acid smut to be eliminated, prolong cold-end equipment life and increase boiler efficiency.

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TABLE I: ADDITIVE MATERIALS

COMPOUND	ALKALINITY	PARTICLE SIZE
calcium hydroxide	high	325 mesh
magnesium oxide	high	325 mesh
sodium aluminate	high	coarse
sodium carbonate	high	coarse
ammonium bicarbonate	high (ammonia donor)	
activated alumina	moderate	325 mesh
expanded vermiculite	moderate	100 mesh
silica	low	submicron

TABLE II: RATE OF ACID DEPOSITION: UNIT A

Additive	Feeder Setting	Feed Rate	Acid deposition, $10^3 \times \text{mg H}_2\text{SO}_4$ $\times \text{min}^{-1} \times \text{in}^{-2}$ at temperature			
			360F	300F	240F	180F
None	---	---	2.1	7.4	12.2	15.4
Ammonium bicarbonate-silica	100%	391b/hr	1.6	2.1	2.7	2.7
	70	27	1.6	1.6	2.7	3.2
	50	13	2.1	2.7	5.3	6.9
	40	4	2.1	3.2	4.3	5.3
Alumina-silica	100	13	2.1	3.2	4.3	5.3
	60	8.6	2.1	4.8	6.4	13.3
	50	2.6	2.1	3.7	6.4	8.0

TABLE III:
ACID DEPOSITION BY LAND METER, UNIT D CONE

Feed Rate, lb Al_2O_3 - SiO_2 /hr	Dew Point, F	Temp of Max Rate of Acid Build-up, F	Maximum Rate of Acid Build-up, $\mu\text{amp/min}$
blank	270	235	210
3.7	255-260	235	100
4.5	260	215	40
9.2	255	195	18

TABLE IV: SURFACE COVERAGE

Additive	Coverage of CERL Probe
SiO_2	even (best)
MgO	even
Ca(OH)_2	even
vermiculite	spotty
Na aluminate	spotty
Na_2CO_3	spotty
$\text{Al}_2\text{O}_3 + \text{SiO}_2$	even

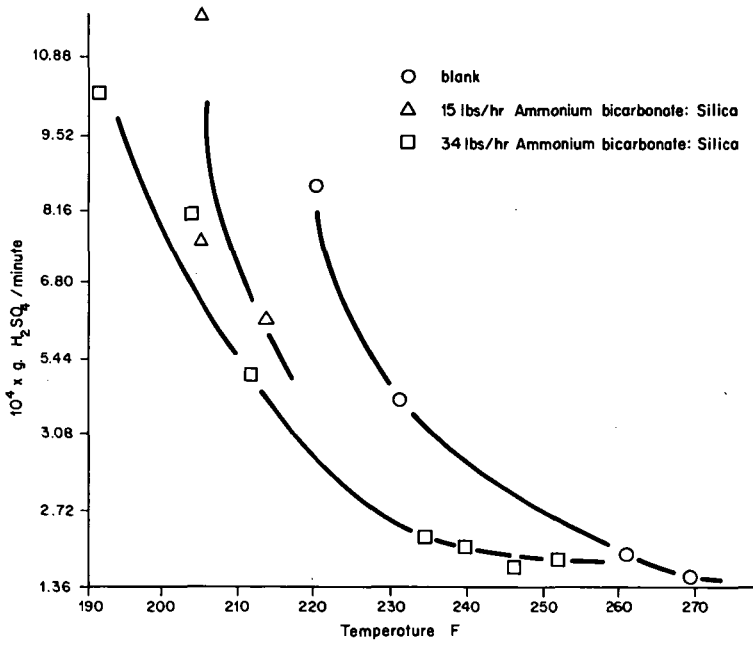


Figure 2. Acid Deposition; Unit B

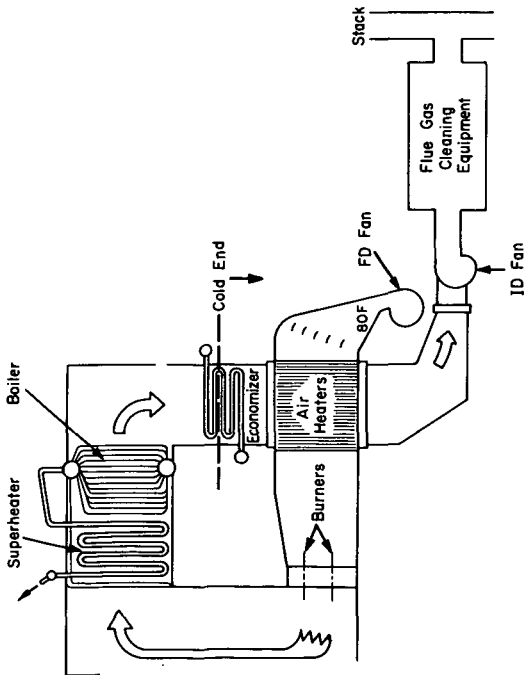


Figure 1. The Cold End

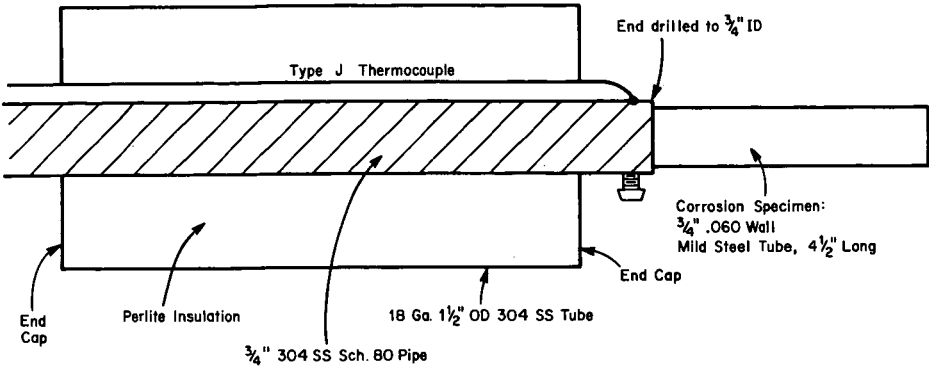


Figure 4. Corrosion Probe

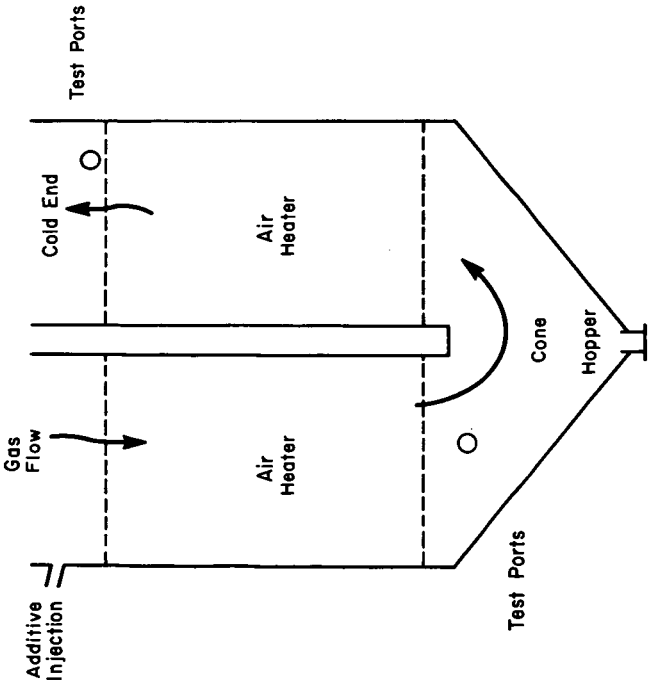


Figure 3. Air Heater Configuration, Unit D

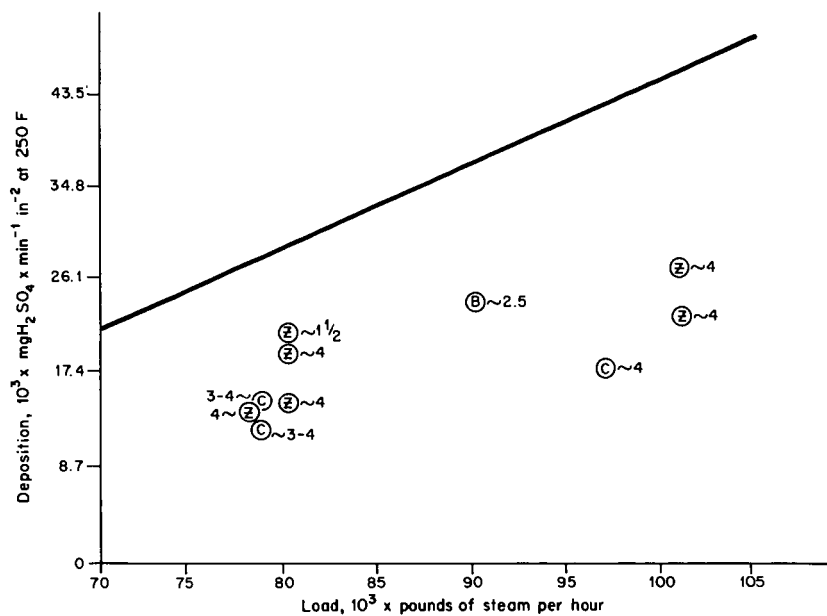


Figure 6. Acid Deposition, Low Feedrates, Unit F

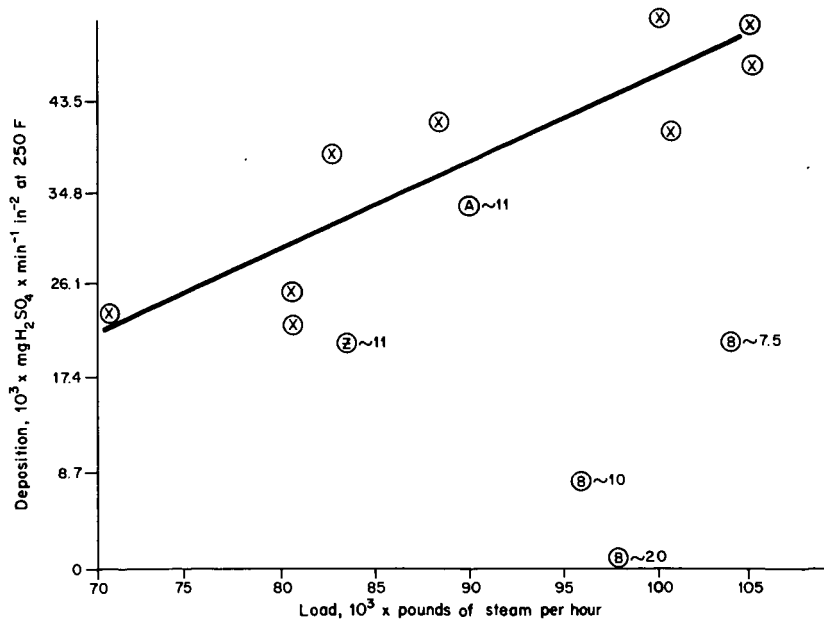


Figure 5. Acid Deposition, High Feedrates, Unit F

KEY TO FIGURES 5 and 6

Symbol	Composition
A	SiO_2
B	MgO
C	Ca(OH)_2
X	Control
Z	$\text{Al}_2\text{O}_3 + \text{SiO}_2$

Control Runs

Feedrates as shown, in pounds per hour.

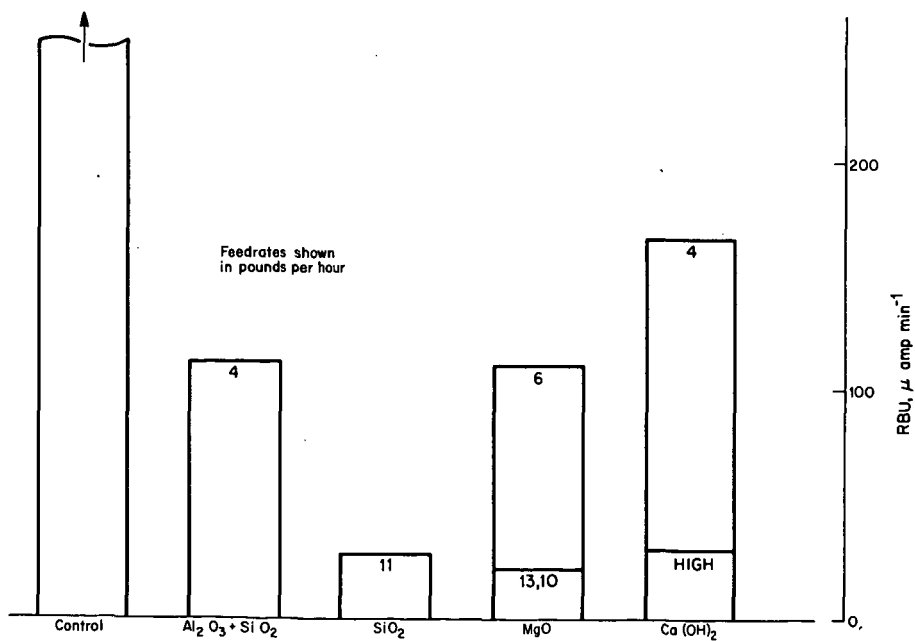


Figure 7. Rate of Acid Build-Up, Unit F